

Geochemistry of the Floridan Aquifer System in Florida and in Parts of Georgia, South Carolina, and Alabama

By CRAIG L. SPRINKLE

REGIONAL AQUIFER-SYSTEM ANALYSIS—FLORIDAN AQUIFER SYSTEM

U.S. GEOLOGICAL SURVEY PROFESSIONAL PAPER 1403-I



Carolina, the rocks making up the aquifer system dip gently toward the sea. In Florida, the formations generally dip away from the positive structural features shown in figure 8 and dip toward the negative features. Development of the structures affecting the aquifer system began in the Early Cretaceous and extended through the late Tertiary.

The rocks of the aquifer system in peninsular Florida were deposited in shallow marine environments typified by the modern-day Bahama Banks. The nearshore intertidal deposits of coquina and coarse-grained limestones may grade laterally into lagoonal and subtidal micrites, locally containing peat and evaporites. In some units, bedded evaporites (primarily anhydrite or gypsum) that may have formed in sabka or tidal flat environments are present. The deep-water limestones are characteristically fine grained and fossil bearing, with only trace amounts of noncarbonate minerals.

Throughout most of the Paleocene and Eocene, deep-sea environments separated the northern Florida peninsula from panhandle Florida, Alabama, and Georgia. Into this trough were carried continental sediments from the north and northwest. Thus, the shallow marine carbonates of the Cedar Keys, Oldsmar, and Avon Park Formations grade progressively northward into limy muds, silts, and sands. During the late Eocene, a major transgression occurred and the Ocala Limestone was deposited over nearly all the region shown in figure 1. The Ocala is commonly a soft, chalky coquina containing minor chert and dolomite locally. This formation has high permeability throughout most of the study area; in fact, most of the water that discharges from the aquifer system comes from springs in the Ocala Limestone (Bush, 1982; Bush and Johnston, 1988). After the late Eocene, continentally derived sand, silt, and clay again were deposited with carbonates in Alabama, Georgia, and northern Florida. In peninsular Florida, the Suwannee Limestone was deposited in a shallow marine environment during the late Oligocene. Where present, the Suwannee Limestone is also a highly productive water-bearing formation.

During the early Miocene, parts of the region underwent cycles of emergence and submergence beneath the sea. The Tampa Limestone was deposited during this period, and in west-central Florida it contains both marine and freshwater limestones. In areas where the sea did not retreat, the Tampa Limestone merges without definite boundary into the overlying Hawthorn Formation; in emergent areas, an unconformity is present between these units. The Hawthorn Formation is a thick sequence of interbedded clay, sand, limestone, sandy phosphatic limestone, and marl. The Hawthorn is present over more than 50 percent of the area underlain

by the Floridan aquifer system and is the major upper confining unit for the system.

MINERALOGY

The matrix of the Floridan aquifer system is composed primarily of calcite and dolomite, with minor gypsum, apatite, glauconite, quartz (or chert), clay minerals (kaolinite and montmorillonite?), and trace amounts of metallic oxides and sulfides. Locally, measurable amounts of peat are present as thin (1–5 millimeters; mm) layers in the limestone.

MAJOR MINERALS

Calcite, the most abundant mineral in the Floridan aquifer system, ranges in composition from stoichiometric calcite (CaCO_3) to magnesian calcite ($\text{Ca}_{0.96}\text{Mg}_{0.04}\text{CO}_3$) (Hanshaw and others, 1971, table 1). The magnesium content of calcite from aquifer cores in Waycross, Ga., and Polk City, Fla., ranged from 0 to 2.7 mole percent Mg, with three of four samples less than 1 percent. Although cores of the entire Floridan aquifer system have not been systematically analyzed, "magnesian calcites probably account for less than 0.1 percent of the [Floridan] limestones by weight" (Plummer, 1977, p. 802), owing to the instability of magnesian calcites relative to stoichiometric calcite in fresh or slightly saline water. Other elements present at trace levels in calcite are sodium, strontium, iron, and manganese. Data on iron and manganese content of calcite from the aquifer system are scarce; sodium and strontium may be present in calcite in concentrations as high as 440 and 600 parts per million (ppm) (Mettrin, 1979), respectively, depending on the aqueous environment during formation of the mineral. The sodium and strontium contents of calcite analyzed by Mettrin (1979) averaged less than 200 ppm and less than 500 ppm, respectively; these values were interpreted by Randazzo and others (1983) to indicate a brackish ground-water environment of diagenesis of middle and upper Eocene rocks (Upper Floridan aquifer) in west-central Florida.

The amount of dolomite in the aquifer system varies both laterally and vertically within and between formations. In a core obtained from a deep test well near Polk City, Polk County, Fla. (pl. 1), dolomite accounted for about 8 percent of the rocks of the Upper Floridan aquifer, about 95 percent of the rocks of the underlying confining unit, and about 9 percent of the rocks penetrated in the Lower Floridan aquifer (A.S. Navoy, U.S. Geological Survey, written commun., 1982). Near Waycross, Ga. (pl. 1), where the base of the Upper Floridan aquifer is also the base of the aquifer system, cores and cuttings from a deep test well were about 30 percent

dolomite (Matthews and Krause, 1984, pl. 1). In south-central Georgia and eastern Alabama, the aquifer system is composed entirely of the Ocala Limestone, and dolomite is absent from the system. Within the aquifer system, dolomite ranges in composition from stoichiometric dolomite ($\text{CaMg}(\text{CO}_3)_2$) to low-magnesium dolomite ($\text{Ca}_{1.12}\text{Mg}_{0.88}(\text{CO}_3)_2$) (Randazzo and Hickey, 1978, p. 1178). This variability in composition of dolomite undoubtedly affects its solubility in ground water. Recent petrographic studies by Cook (1984) indicate that the nonstoichiometric centers of dolomite crystals in the Floridan aquifer system have dissolved while the more stoichiometric rims have remained. Unfortunately, little is known about the location and volumetric occurrence of nonstoichiometric dolomite in the aquifer system. Furthermore, quantitative data on the solubility of nonstoichiometric dolomite are lacking. These factors prevent making more than general estimates of the saturation state of dolomite in the Floridan aquifer system.

The origin of dolomite within the aquifer system is a subject of continuing study (Hsu, 1963; Hanshaw and others, 1971; Randazzo and others, 1977; Randazzo and others, 1983). The magnesium content of dolomite is often cited as an indicator of the diagenetic environment during formation of the mineral (for example, Land, 1973; Veizer and Demovic, 1974; Folk and Land, 1975). Other elements that are present in dolomite in trace amounts are also used to indicate environments of diagenesis, especially strontium and sodium. Owing to its large ionic size, the strontium ion primarily replaces the calcium ion in the CaCO_3 "layer" of dolomite (Behrens and Land, 1972). Strontium has been determined in concentrations as high as 288 ppm in Eocene dolomite of west-central Florida (Sarver, 1978). Sodium ions are smaller than calcium ions but much larger than magnesium ions; thus, sodium should substitute primarily for calcium in the CaCO_3 "layer" of dolomite, although Land and Hoops (1973) suggested that sodium could substitute equally for either calcium or magnesium in dolomite. Sodium has been determined in concentrations as high as 1,200 ppm in Eocene dolomite of west-central Florida (Mettrin, 1979). The high concentrations of sodium in dolomite of the Floridan aquifer system appear to indicate that the dolomite formed in moderately saline solutions (Randazzo and others, 1983). The magnesium, sodium, and strontium contents of dolomites in the aquifer system have been used in conjunction with rock textures as evidence for multiple diagenetic episodes in the development of the Upper Floridan aquifer in west-central Florida (Randazzo and others, 1977; Randazzo and Hickey, 1978; Randazzo and others, 1983).

The stable isotopes ^{13}C and ^{18}O in calcite and dolomite are also used as indicators of the diagenetic history of the rocks. The ^{13}C content provides evidence about the

sources of CO_2 available for dissolution and reprecipitation of the carbonate phases. The ^{18}O content of the carbonates is related to the aqueous environment of diagenesis, especially the temperature of the aquifer system during the last diagenetic episode. Available stable isotope data for dolomite and calcite from the aquifer system are presented in table 2. Many stable isotope data from carbonates have been reported as concentration relative to the Pee Dee belemnite (PDB), but the oxygen data in table 2 are reported relative to Vienna SMOW. The relation between these two standards is

$$\delta^{18}\text{O}_{\text{PDB}} = (0.97006 \delta^{18}\text{O}_{\text{SMOW}}) - 29.94.$$

Except for two isotopically heavy samples, calcite ranges in $\delta^{13}\text{C}$ from about -0.5 to $+0.5$ ‰ (permil). The calcite samples from the deep zones (about 1,000 ft) of the Waycross and Green Swamp test wells may reflect the original seawater environment of formation, since the calcites have $\delta^{13}\text{C}$ values similar to surface seawater (Kroopnick and others, 1972). Methane has been detected in water samples from the 1,900- to 1,970-ft zone in the Waycross well (table 4), so it is also possible that the heavy $\delta^{13}\text{C}$ calcites in that well may result from in situ formation of calcite with isotopically heavy CO_2 produced by anaerobic bacteria. The lighter $\delta^{13}\text{C}$ calcites listed in table 2 were probably formed from isotopically light ground water.

The $\delta^{18}\text{O}$ content of calcites began to be used to determine paleotemperatures after Urey presented his classic paper in 1946 (Urey, 1947; Hoefs, 1980, p. 147-152). Attempts to use the $\delta^{18}\text{O}$ content of calcite samples from the Floridan aquifer system to estimate the paleotemperatures of ground water is hindered by several problems, the most intractable being the timing and pattern of diagenesis and the amounts of calcite precipitated in each diagenetic episode. For example, using oxygen isotopic fractionation factors given in Friedman and O'Neil (1977, fig. 13), the lowest and highest $\delta^{18}\text{O}$ values for calcite in table 2, and two values for $\delta^{18}\text{O}$ in ground water (fig. 3B), the following ranges in ground-water temperature (T) are obtained:

$\delta^{18}\text{O}$ calcite	$\delta^{18}\text{O}$ ground water	Δ calcite-ground water	T equilibrium
+26.7 ‰	-2.5 ‰ (well 3)	29.2 ‰	20 °C
+29.0 ‰	-3.6 ‰ (well 4)	32.6 ‰	12 °C

If the ground-water temperature is assumed to be 20 °C, the calcite data could be used to estimate the $\delta^{18}\text{O}$ value of ground water:

$\delta^{18}\text{O}$ calcite	T equilibrium	Δ calcite-ground water	$\delta^{18}\text{O}$ ground water
+26.7 ‰	20 °C	29.5 ‰	-2.8 ‰
+29.0 ‰	20 °C	29.5 ‰	-0.5 ‰

TABLE 2.—Carbon and oxygen isotopic data for carbonate minerals from the Floridan aquifer system

[Values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in permil (‰) relative to Pee Dee belemnite and Standard Mean Ocean Water, respectively. Dashes indicate isotope not measured]

Sample number	Sample location	Dolomite		Calcite	
		$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
1	Well 274 ¹ (near Brooksville, Fla.)	-7.5	+31.3	-0.4	+27.3
2	Well 519 ¹ (at Frostproof, Fla.)	-2.8	+32.7	+0.6	+28.9
3	Well 4750 ¹ (near Palmdale, Fla.)	-3.1	+32.2	-0.4	+26.7
4	Well 275 ¹ (at Groveland, Fla.)	---	---	+0.5	+27.3
5	Core from 14-meter depth near Inglis, Fla. ¹	+1.0	+33.4	---	---
6	Outcrop near Inglis, Fla. ¹	+0.7	+33.4	---	---
7	Outcrop at Inglis Canal Bridge ¹	+0.1	+33.2	---	---
8	Core, 763–773 feet, TW-1, ² near Waycross, Ga. ³	---	---	-0.7	+28.1
9	Core, 905–915 feet, TW-1, near Waycross, Ga.	-1.8	+32.7	---	---
10	Core, 1,056–1,066 feet (vein), TW-1, near Waycross, Ga.	-0.4	+32.3	---	---
11	Core, 1,056–1,066 feet (matrix), TW-1, near Waycross, Ga.	+2.5	+33.6	---	---
12	Core, 1,232–1,248 feet, TW-1, near Waycross, Ga.	---	---	+2.1	+29.0
13	Core, 1,375–1,385 feet, TW-1, near Waycross, Ga.	+1.8	+32.9	---	---
14	Core, 381–396 feet, Green Swamp TW, near Polk City, Fla.	-3.0	+31.9	---	---
15	Core, 544–561 feet, Green Swamp TW, near Polk City, Fla.	+1.2	+33.9	---	---
16	Core, 757–769 feet, Green Swamp TW, near Polk City, Fla.	+2.6	+33.2	---	---
17	Core, 955–978 feet, Green Swamp TW, near Polk City, Fla.	+3.0	+33.4	+0.5	+28.5
18	Core, 1,570–1,578 feet, Green Swamp TW, near Polk City, Fla.	+2.0	+31.8	---	---
19	Core, 1,959–1,968 feet, Green Swamp TW, near Polk City, Fla.	---	---	+2.0	+27.0
20	Core, 226 feet, test well MS, near Chiefland, Levy County, Fla.	+2.2	+34.4	---	---
21	Core, 277 feet, test well MS, near Chiefland, Levy County, Fla.	+0.6	+34.6	---	---
22	Core, 203 feet, test well 124, near Inglis, Levy County, Fla.	+2.6	+33.6	---	---
23	Core, 216 feet, test well TR21–2, near Lecanto, Citrus County, Fla.	+2.8	+33.7	---	---
24	Core, 175 feet, test well near Homosassa Springs, Citrus County, Fla.	+1.9	+33.1	⁴ +0.3	⁴ +33.1
25	Core, 250 feet, test well near Homosassa Springs, Citrus County, Fla.	+2.2	+34.7	---	---
26	Core, 452 feet, test well TR19–3, near Tooke Lake, Hernando County, Fla.	+2.0	+33.5	---	---
27	Core, 261 feet, test well TR17–1, near Hudson, Pasco County, Fla.	-2.6	+32.4	---	---
28	Core, 341 feet, test well TR6–3, near Bee Ridge, Sarasota County, Fla.	-3.2	+34.2	---	---
29	Core, 245 feet, test well TR4–2, near South Venice, Sarasota County, Fla.	-2.7	+33.6	---	---
30	Core, 364 feet, test well 101, near Bay Lake, Lake County, Fla.	+0.6	+34.0	---	---
31	Core, 642 feet, test well TR11–2, near Mango, Hillsborough County, Fla.	-1.8	+32.2	-2.4	⁴ +32.5

¹ Data from Hanshaw and Back (1972, table 2).² TW, test well.³ Precision of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data is ± 0.2 permil. Pieces of core were selected to be monomineralic and ground to fine powder (-250 mesh). Secondary cements, if present, could affect the isotopic values reported.⁴ Values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for calcite are questionable. Core samples were approximately 98 percent dolomite. Calcite could not be quantitatively extracted prior to isotopic analysis.

The heavier $\delta^{18}\text{O}$ estimated from ground water is about 2 ‰ more enriched than the heaviest modern-day ground-water samples from Georgia (fig. 3B). These estimates appear to indicate that recharge was derived from somewhat colder precipitation than occurs today.

Determining the stable isotope content of dolomite is a more complex problem because (1) the fractionation factors between water and dolomite are not known for temperatures below about 100 °C and (2) the influence of the isotopic content of the carbonate precursor is difficult to establish (Land, 1980, p. 88–93). The stable isotope data from dolomites presented in table 2 show a narrow range of values of $\delta^{18}\text{O}$ and a somewhat wider range of $\delta^{13}\text{C}$ values. Hanshaw and Back (1972, p. 147) concluded that dolomite with $\delta^{13}\text{C}$ values less than -1 ‰ had

formed in a ground-water environment that contained isotopically light bicarbonate ions, whereas dolomite with $\delta^{13}\text{C}$ values in the range of -1 to $+3$ ‰ apparently formed in a more marine environment. The isotopic data from the Waycross and Green Swamp test wells show a general increase in the $\delta^{13}\text{C}$ of carbonates with increasing depth. This is probably related to the development of the freshwater flow system within the aquifer system. At both the Waycross and Green Swamp test wells, the major permeability and greatest volume of freshwater flow occur in the upper few hundred feet of the limestone section. As depth increases, ground-water flow is more sluggish owing to a marked decrease in permeability. The deeper dolomite (and calcite) examined from both wells appear to have formed in a system “closed” to

CO₂-rich meteoric water (which is isotopically light in $\delta^{13}\text{C}$). Thus, the $\delta^{13}\text{C}$ content of the deep dolomite from the two test wells may have been inherited from preexisting carbonates. Assuming the dolomite inherited the isotopic content of a precursor carbonate phase (calcite?), the fractionation of $\delta^{18}\text{O}$ between the dolomite and the "coexisting" calcite (samples 12, 13, and 17, table 2) is in the appropriate range (+4 to +5 ‰) for low-temperature diagenesis (Land, 1980, p. 90–92).

MINOR MINERALS

Gypsum is an important minor mineral in the Floridan aquifer system. Miller (1986) used the presence or absence of intergranular gypsum as an indicator to define confining units of the system. Cook (1984) and Thayer and Miller (1984) have used gypsum morphology and its association with sedimentary structures in dolomitic facies of the Avon Park Formation to determine depositional environments and diagenetic history of the rocks. Within the modern-day freshwater flow system, the continuous dissolution of gypsum leads to incongruent dissolution of dolomite and calcite precipitation (Plummer, 1977). Plummer and others (1983) used the sulfate produced from gypsum dissolution as a progress variable to study changes in Ca^{2+} , Mg^{2+} , $\delta^{13}\text{C}$, and pH along a ground-water flow path in the Upper Floridan aquifer. Isotopic ratios of $\delta^{34}\text{S}$ in dissolved sulfate (SO_4^{2-}) and from sulfate in gypsum have been used to describe some of the redox reactions of the aquifer system (Pearson and Rightmire, 1980; Rye and others, 1981; Plummer and others, 1983). The data on sulfur isotopes in gypsum from the aquifer system show that the sulfate was of marine origin (table 3), and not derived from oxidation of sulfides. Some of the gypsum samples listed in table 3 are heavier in $\delta^{34}\text{S}$ than modern marine water, indicating the gypsum may have formed in a reducing environment (Nielsen, 1979, p. 291–294). Data on the trace element composition of gypsum from the aquifer system are scarce; this lack of data may not be a serious obstacle in interpreting the geochemistry of the system, however, because the mineral tends to vary little in composition (Stewart, 1963, table 22; Deer and others, 1966, p. 466).

The minor mineral apatite (predominantly carbonate fluorapatite) is a potential source of calcium, fluoride, bicarbonate, phosphate, trace metals, and radionuclides in ground water of the Floridan aquifer system. Apatite is present in trace amounts throughout the system, varying in abundance areally and by formation. Over the entire region, apatite is most abundant in the Tampa Limestone in southwestern Florida. Less common occurrences of phosphatic minerals are in the upper Eocene and Oligocene limestones in southern Georgia and in

northern and central Florida. In a few areas, the Hawthorn Formation, which makes up the major part of the upper confining unit of the aquifer system, and overlying Pliocene sediments are rich in phosphatic minerals containing uranium and other trace metals (Altschuler and others, 1958; Riggs, 1979). In recharge areas, ground-water leakage through the Hawthorn could increase Ca^{2+} , PO_4^{3-} , F^- , trace metal, and radionuclide concentrations in the Upper Floridan aquifer.

The two principal mineral varieties of silica in the aquifer system are chert (chalcedony) and quartz (detrital sand grains); opaline varieties of silica (tests from marine organisms) are rare in the limestones (Miller, 1986). Throughout most of peninsular Florida, the aquifer system contains very little detrital quartz or chalcedony (probably less than 1 percent everywhere). In panhandle Florida, southern Alabama, and Georgia, the aquifer system contains appreciable quantities of detrital quartz as the limestones grade laterally into limy sands and silts. In these areas aluminosilicate minerals, mostly clay minerals, are also relatively abundant.

Very little information on the identity of aluminosilicate (clay) minerals in the Floridan is available. Numerous workers mention "glauconite," "clay," or "clayey residues" in descriptions of cores and drilling chips, but few X-ray or other analytical data on these minerals are available. A few X-ray diffractograms were made during this study of cores of the Avon Park Formation in west-central Florida; these diffractograms indicated weak 7.1 angstrom (Å) peaks (kaolinite) and trace 15 Å peaks (montmorillonite?). The diffractograms also indicated that small amounts of potassium feldspar are present in zones of the Avon Park Formation. Where present, glauconite may be weathering to yield trace amounts of silica, aluminum, iron, and potassium to ground water. Riggs (1979, p. 216–218) discusses aluminosilicate weathering of Miocene rocks in central Florida; similar weathering processes (and minerals?) probably occur in the older rocks of the Floridan where the system is unconfined. According to Riggs (1979, p. 217), both phosphatic and siliceous mineral phases increase in aluminum content as weathering proceeds. He states:

In central Florida, the unaltered calcium phosphate occurs as a carbonate fluorapatite which grades upward to calcium-aluminum phosphate, occurring as crandallite and millisite. These change upward to the pure aluminum phosphate, wavellite. . . . The clay minerals have a similar gradational sequence. The clay minerals at the base consist of a montmorillonite-attapulgite assemblage which grades upward to a montmorillonite assemblage overlain by a montmorillonite-kaolinite assemblage and finally to a kaolinite assemblage.

This weathering sequence may affect silicates in the Floridan but not phosphatic minerals because of the abundance of carbonate minerals in the aquifer. Nathan and Sass (1981) have described the stability of carbonate fluorapatite in the presence of carbonate minerals; within

TABLE 3.—Sulfur isotopic content of gypsum (anhydrite) from the Floridan aquifer system
[In permil relative to troilite from Canyon Diablo meteorite]

Location	$\delta^{34}\text{S}$	Reference
Five gypsum samples from central Florida	+19 to +22	Pearson and Rightmire (1980, p. 246)
Core, test well, Waycross, Ga., 1,375–1,385 feet	+21.4	
Core, test well, Waycross, Ga., 1,723–1,733 feet	+22.2	
Core, test well, Green Swamp, Fla., 1,021–1,036 feet	+22.6	
Core, test well, Green Swamp, Fla., 1,894–1,903 feet	+23.2	
Sulfate from modern ocean water	+20	Hoefs (1980, p. 117)

the aquifer system, ground-water pH normally is in the range 7.0 to 8.5, which is an exceptionally stable environment for carbonate-fluorapatite. The possibility that weathering reactions similar to those described above might control the aluminum and silica concentrations in the Upper Floridan aquifer is discussed in greater detail later in this paper. Regardless of the actual minerals involved, weathering and diagenesis of aluminosilicates within the aquifer system are slow processes and, except possibly for potassium and silica, are relatively insignificant controls on the major element chemistry of ground water in the aquifer system.

The clay minerals in the aquifer system may have a significant role in controlling sodium and calcium concentrations, however, where cation exchange occurs. The importance of Ca^{2+} for 2Na^{+} exchange to produce sodium bicarbonate solutions in regional aquifers has been described by Renick (1924a), Foster (1950), Thorstenson and others (1979), Chapelle and Knobel (1983), and Lee (1985). The occurrence of sodium bicarbonate water within the Floridan aquifer system is limited to a small area of western panhandle Florida (pl. 9; also Barraclough and Marsh, 1962). The effects of cation exchange on the water chemistry of the aquifer system are discussed in following sections.

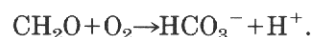
Trace amounts of sulfide minerals (primarily pyrite or marcasite) are present at depth throughout the system. These sulfide minerals generally form as a result of bacterially mediated sulfate reduction which generates hydrogen sulfide (H_2S), the source of rebarbative odors in many untreated water supplies. Hydrogen sulfide is a weak acid, so that the predominant species containing reduced sulfur in solution depends on pH. The activities of H_2S and HS^{-} are related by an acid dissociation constant $\text{pK}_{25^\circ\text{C}} = 6.96$. This means that at 25°C and pH of 6.96, the activities of H_2S and HS^{-} in solution are

equal. In the normal range of pH conditions in the Upper Floridan aquifer (about pH 7.0 to 8.5), the dominant reduced-sulfur species is bisulfide. Sulfide (S^{2-} usually is present in the Upper Floridan only in minute amounts: for example, at pH of 7 and HS^{-} ($=\text{H}_2\text{S}$) concentration of 1 milligram per liter (mg/L), S^{2-} concentration is approximately 10^{-7} mg/L. This is sufficient, however, to precipitate many trace metal sulfides owing to the extremely low solubility of these minerals. Once formed, sulfide minerals are practically insoluble in pure water. However, when oxygen is available to reoxidize the sulfide to sulfate, the mineral can be dissolved. The uniformly low concentrations of trace metals in natural ground water from the Floridan aquifer system is in part related to lack of primary (and soluble) sources of trace metals. The almost ubiquitous formation of H_2S and precipitation of metallic sulfides maintain low trace metal concentrations throughout most of the aquifer system.

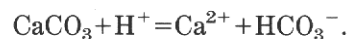
A geochemically important but relatively rare component of the Floridan aquifer system is carbonaceous residue, or peat. This organic material is not abundant in any horizon or rock unit, but occasionally occurs as lamellae or thin layers in the more deeply buried rocks. Some of this organic material is utilized by anaerobic microbes to reduce SO_4^{2-} to S^{2-} via the reaction



where CH_2O is a generalized organic molecule containing the approximate ratio C:H:O of typical carbohydrates in sediments. The peat can also be readily oxidized by aerobic microbes, which convert organic carbon to HCO_3^{-} via the reaction



Note that both of the above reactions produce acidity (H^{+}) and bicarbonate ion. The acidity may then be consumed by reaction with calcite:



If the acidity reaction exists, then a net 3HCO_3^{-} will be produced for each mole of SO_4^{2-} reduced, or 2HCO_3^{-} for each mole of CH_2O oxidized by O_2 . The HCO_3^{-} produced may be isotopically light in carbon ($\delta^{13}\text{C}$ about -25 ‰) and, depending on quantities of peat oxidized, can measurably affect the ^{13}C content of ground water in the Upper Floridan aquifer. Even where the aquifer system is too anaerobic or too sulfate deficient to sustain sulfate-reducing bacteria, the peat may still be oxidized by heterotrophic bacteria. In the anaerobic environment, the primary byproducts of heterotrophic oxidation are molecular hydrogen and acetate, both of which are consumed by methanogenic bacteria to produce meth-

ane. Measurements of dissolved gases in water samples indicate that methane is present in the aquifer system in Georgia and Florida (table 4; Ehrlich and others, 1979). The methane produced in the anaerobic parts of the aquifer system is not confined there and could migrate upward into more oxidizing environments. In an oxidizing zone, the methane is converted by bacteria to CO_2 , which could have a very low ^{13}C content ($\delta^{13}\text{C}$ ranging from -65 to -85 ‰ (Hoefs, 1980, fig. 47)).

The significance of reduced carbon sources and their isotopic contents in developing geochemical reaction models of the Upper Floridan aquifer in southwestern Florida is discussed in detail by Plummer and others (1983). Their calculations using $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ showed that where the aquifer system is confined (such as in southwestern Florida), input of reduced carbon was affecting the carbon isotope chemistry. As a result of the work by Plummer and others (1983), the methodology is available for quantitative interpretation of redox reactions involving carbon in regional aquifer systems. However, application of their methods to other parts of the Floridan aquifer system must await availability of data on environmental isotopes, dissolved gases, and aquifer mineralogy.

HYDROLOGY

The Floridan aquifer system generally consists of an Upper and Lower Floridan aquifer separated by a less permeable confining unit of highly variable properties (Miller, 1986). The upper and lower aquifers were defined on the basis of permeability; thus, aquifer boundaries in many places do not coincide with boundaries for either time-stratigraphic or rock-stratigraphic units. The Upper Floridan aquifer is present throughout the region and contains units ranging in age from middle Eocene to early Miocene (Miller, 1982a, 1982c, 1986). Several formations are included in the Upper Floridan aquifer, primarily the Tampa, Suwannee, and Ocala Limestones and the Avon Park Formation. The Lower Floridan aquifer is not present in parts of northwestern Florida and in Georgia inland from the coast (fig. 9; Miller, 1986). In these areas, there is little permeability contrast within the aquifer system. Where present, the Lower Floridan aquifer may consist of Paleocene to middle Eocene formations, but consists primarily of the Oldsmar and Cedar Keys Formations.

The major features of the regional flow system of the Floridan can be seen on potentiometric surface maps. An estimated potentiometric surface map of the Upper Floridan aquifer prior to development was made by Johnston and others (1980); a modified version of the map is shown in figure 10. The potentiometric surface shown in figure 10 represents an average, undeveloped condi-

tion of the Upper Floridan made from the best information and estimates available (Johnston and others, 1980). Several important hydraulic features of the flow system are evident. Depressions in the potentiometric surface indicate areas of natural discharge that occur along stream channels or near springs; simulation of the aquifer system indicates that almost 90 percent of natural discharge is to rivers and springs (Bush and Johnston, 1988). Along the coast of Florida, low heads generally indicate nearshore springs or seepage from submarine outcrops; simulation of predevelopment conditions indicates that less than 5 percent of the total discharge is directly into the sea. The high heads along the Georgia coast result from thick confinement by the Hawthorn Formation, and freshwater flow extends as far as 50 miles (mi) offshore (Johnston and others, 1982) in that area. The potentiometric high areas shown in figure 10 are areas of potential recharge to the aquifer system. The amounts of actual recharge can vary widely, however, owing to varying thicknesses of aquifer confinement and magnitude of local downward hydraulic gradients (Bush, 1982).

The Floridan aquifer system is remarkably productive. The exceptionally high permeability of some units within the aquifer system are the result of solutional enhancement of high primary permeabilities of the coquinas and fossiliferous limestones. As a result of the wide variation in hydrogeologic conditions in the Upper Floridan aquifer, transmissivity varies by more than three orders of magnitude (Bush and Johnston, 1988, pl. 2). Transmissivities of more than 1,000,000 square feet per day (ft^2/d) occur in the karst areas of west-central and northwestern Florida. The variability of depositional environments when the limestones were formed has also produced low-permeability units that are areally extensive—for example, in the Gadsden County area of northern Florida. In this area, transmissivities are less than 1,000 ft^2/d and vertical head gradients as large as 40 ft are maintained by low-permeability limestones in the Upper Floridan (Rosenau and Milner, 1981). Extending in a northeasterly direction from Gadsden County toward Candler County, Ga., is a series of grabens which markedly affect the transmissivity of the aquifer system. These geologic structures, collectively referred to as the Gulf Trough (fig. 8; Herrick and Vorhis, 1963; Gelbaum, 1978), have the principal effects of locally reducing the thickness of the limestone section, placing low-permeability clastics adjacent to highly permeable limestones, and creating steep hydraulic gradients in the vicinity of the grabens (fig. 10; Pascale and Wagner, 1981; Krause and Randolph, 1989). The Gulf Trough feature has created a damming effect on the southeasterly flow of ground water in the Floridan aquifer system,